

First-principles calculation of electronic structure, chemical bonding and optical properties of β -AgBiS₂

Y. Zhang^a, J. Guo^a, Y. W. Zhang^a, Q. Y. Zou^{a,b,c,*}, S. R. Zhang^{d,*}, Q. Lai^e

^aCollege of Chemistry and Materials Engineering, Huaihua University, Huaihua 418008, China

^bKey Laboratory of Research and Utilization of Ethnomedicinal Plant Resources of Hunan Province, Huaihua University, Huaihua 418008, China

^cKey Laboratory of Hunan Higher Education for Western Hunan Medicinal Plant and Ethnobotany, Huaihua University, Huaihua 418008, China

^dSchool of Physics, Electronics and Intelligent Manufacturing, Huaihua University, Huaihua 418008, China

^eCollege of Vanadium & Titanium, Panzhihua University, Panzhihua 617000, China

We investigated the structural, electronic, chemical bonding, and optical properties of β -AgBiS₂ crystal by using the Perdew-Burke-Ernzerhof (PBE) functional and the hybrid functional Heyd Scuseria Ernzerhof (HSE) within the DFT formalism. The electronic band structures obtained by both methods indicate that β -AgBiS₂ is an indirect band gap semiconductor with band gap of 0.571 and 1.025 eV, respectively. The electron density difference and Mulliken overlap population show that the Ag-S bonds and Bi-S bonds are both ionic bonds. The calculated optical absorption spectrum prove that β -AgBiS₂ is a promising material for solar photovoltaic conversion.

(Received May 8, 2023; Accepted August 10, 2023)

Keywords: AgBiS₂, First-principles, HSE06, Electronic structure, Optical properties

1. Introduction

Matildite (β -AgBiS₂) possesses excellent physical properties and has great potential for applications in different fields such as thermoelectrics, photocatalysis, and solar photovoltaics, which has attracted great attention of many researchers. In recent years, a lot of experimental explorations of β -AgBiS₂ have been carried out, and the researches involve the preparation of materials and functional devices, as well as the related property characterization and performance testing [1-7]. Compared to the large number of experimental explorations, there are not many theoretical studies on β -AgBiS₂ crystals. We note in particular several interesting theoretical works: Francesc Illas et al. have investigated the origin of photoactivity in AgBiS₂ by first-principles calculations [8], Shugo Suzuki and Makoto Tsuyama studied the electronic and optical properties of this material [9], Xiaotian Wang et al. have performed a systematic theoretical study of the

* Corresponding author: zouqioyu@126.com
<https://doi.org/10.15251/CL.2023.208.579>

structural, electronic and thermoelectric properties of β -AgBiS₂ compound Via the FP-APW+lo method [10]. However, these theoretical reports are not uniform in their views on the electronic structure of β -AgBiS₂, and they also lack the study of the chemical bonding properties and the optical absorption spectrum of this material.

Based on the above, our work will further investigate the electronic band structure, density of states, electronic density difference, chemical bonding and optical properties of the material. In the following, we will describe the computational methods and discuss the results.

2. Computational methods

We used the CASTP code [11, 12] to calculate the structural, electronic, chemical bonding and optical properties of β -AgBiS₂ crystal throughout the study. In the geometry optimization process, the effects of exchange–correlation interaction are treated with the generalized gradient approximation (GGA) of Perdrew-Burke-Ernzerh (PBE) [13]. the electron–ion interactions are described by the Vanderbilt-type ultrasoft pseudopotentials (USP) [14], a plane-wave cutoff energy of 330.00 eV in USP is employed, and a grid of $16 \times 16 \times 3$ k points generated according to the Monkhorst–Pack scheme is adopt for the Brillouin-zone sampling. The convergence criteria in the self-consistent iterative process: the total energy difference within 1.0×10^{-6} eV/atom, the maximum Hellmann–Feynman force within 0.01 eV/Å, the maximum stress within 0.02 GPa and the maximum atom displacement within 1.0×10^{-4} Å.

In the subsequent calculation of the electronic structure and optical properties of β -AgBiS₂, we used PBE and the hybrid functional (HSE06) [15], respectively. In calculating the optical properties of this material using the PBE method, a grid of $32 \times 32 \times 6$ k points is used to ensure the reliability of the optical properties. During the calculation of electronic structure and optical properties of this material using the hybrid function HSE06 method, the interaction of valence electrons with ions cores is represented by the norm conserving pseudopotentials [16], a plane-wave cutoff energy of 850.00 eV is employed.

3. Results and discussion

3.1. Structural optimization

As shown in Figure 1, β -AgBiS₂ crystal belongs to the P3-M1 group, which is a hexagonally symmetric structure with experimental values of lattice constants $a = 4.07$ Å, $c = 19.06$ Å [17]. Here, a is the lattice constant in the x or y direction, c is the lattice constant in the z direction. The positions of the ions are expressed in (x, y, z) coordinates with a and c constants as units of length as follows,

Ag ions: (0, 0, 0), (0.3333, 0.6667, 0.672);

Bi ions: (0, 0, 0.5), (0.3333, 0.6667, 0.163);

S ions: (0, 0, 0.253), (0.3333, 0.6667, 0.926), (0.3333, 0.6667, 0.406).

In this work, we use the experimental results mentioned above as the initial values for the geometry optimization. Considering the time cost and accuracy requirements of the calculations, we adopt the GGA-PBE method to optimize the geometry of β -AgBiS₂ crystal. The calculated

lattice constants, along with other reported theoretical and experimental data [8, 17-21] are all listed in Table 1 for comparison. The calculated lattice constants a and c are 4.019 and 18.968 Å, respectively, with 1.15%-1.25% and 0.05%-0.4% deviation from the experimental values, a favorable agreement by DFT standards. We will perform electronic properties and optical absorption spectra calculations based on this geometrically optimized structure.

Table 1. Crystal lattice constant a (Å), c (Å), and the band gap E_g (eV) of β -AgBiS₂ compared to experimental and other theoretical values.

parameters	This work		Other theory			Experiments	
	PBE	HSE	PBE		HSE		
a	4.019		4.0497 ^[8]	4.02 ^[18]		4.066 ^[19]	4.07 ^[17]
c	18.968		19.109 ^[8]	19.05 ^[18]		18.958 ^[19]	19.06 ^[17]
E_g	0.571	1.205	0.42 ^[8]	0.463 ^[18]	1.54 ^[8]	0.9 ^[20]	1.2 ^[21]

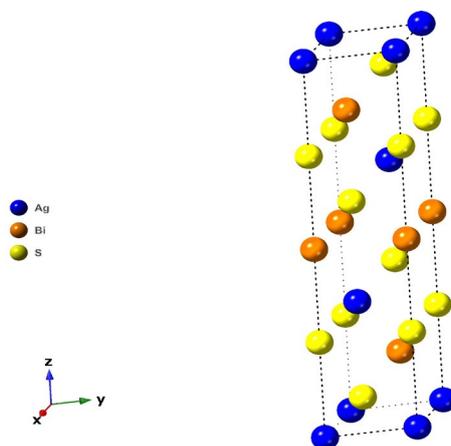


Fig. 1. Crystal structure of β -AgBiS₂ crystal.

3.2. Electronic properties

We calculated the electronic band structure of β -AgBiS₂ crystal by the PBE and HSE06 methods, respectively, and the related results are displayed in Figure 2, from which we can see that the energy band structure diagrams obtained by the two different methods are very similar overall, the valence band maximum is located between the G and K points, while the conduction band minimum is located at the G point, β -AgBiS₂ crystal is an indirect band gap semiconductor, the band gaps obtained by the two different methods are 0.571eV, 1.205eV, respectively. We can noticed that the band gap obtained by the hybrid functional HSE06 method is very close to the experimental value, while the band gap obtained using the GGA-PBE method is significantly smaller than the experimental results, which is due to the fact that the PBE method ignores the continuity of exchange-correlation energy [22].

Figure 3 shows the partial density of states and the total density of states of each atom of β -AgBiS₂ crystal obtained by the generalized gradient approximation (GGA) and hybrid functional HSE06, respectively. As can be seen from the two pictures, the results obtained by the two methods are very similar. The more obvious difference is the larger gap width at energy 0 eV in

the total density of states diagram obtained with the hybrid functional HSE06 method. It can be found that, for β -AgBiS₂, the PBE results show the 4*d* states of cation Ag is highly located, the hybrid functional HSE06 results indicate the degree of localization of 4*d* states of cation Ag and 3*p* states of anion S is decreased. The electron activity is strongest near the Fermi energy level. The electronic density of states distribution shows that the upper valence band is mainly composed of 4*d* states of cation Ag, 6*s* states and 6*p* states of cation Bi, and 3*s* states of anion S, and the lower conduction band is derived mostly from 4*p* states and 5*s* states of cation Ag, 6*p* states of cation Bi, along with 3*p* states of anion S.

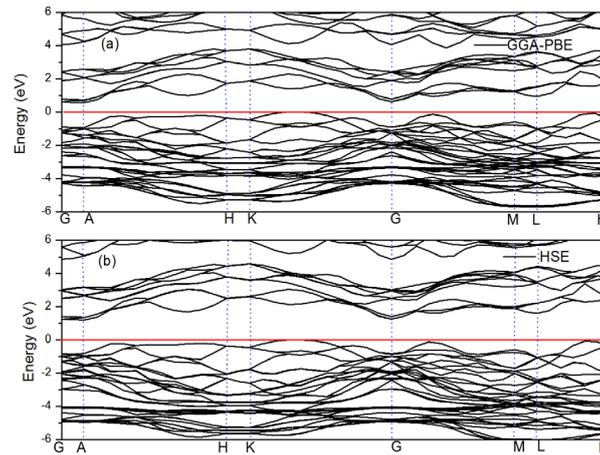


Fig. 2. Band structure of β -AgBiS₂ crystal.

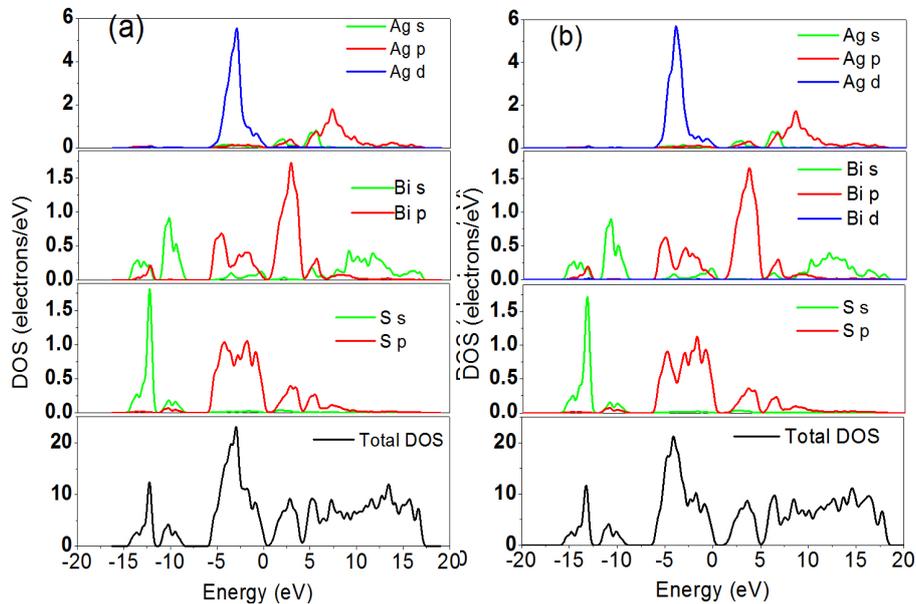


Fig. 3. Total and partial state density of β -AgBiS₂ crystal

The charge density difference diagram presents the gain and loss of electrons when each atom is bound, Figure 4 shows the charge density difference diagram of the (110) crystal plane of β -AgBiS₂ obtained by the hybrid functional HSE06 method, where blue represents the loss of electrons, yellow represents no change, and red represents gain of electrons. It can be found that

both silver and bismuth atoms lost some electrons, while sulfur atoms gained electrons, and in comparison, bismuth atoms lost electrons more severely than silver atoms.

To get more insight into the nature of chemical bonding in β -AgBiS₂ crystal, we calculated the Mulliken charge and bond overlap population using the hybrid functional HSE06 method, and the results are listed in Table 2, it can be found that the bismuth element loses 0.91 e, and the silver element loses 0.24 e, while the sulfur element gained about 0.57 e, all three elements are in ionic state. It can be seen that the overlap population of Ag-S bonds and Bi-S bonds is 0.38 and 0.47, respectively, indicating that both chemical bonds are bonding states and have strong ionic bonding properties.

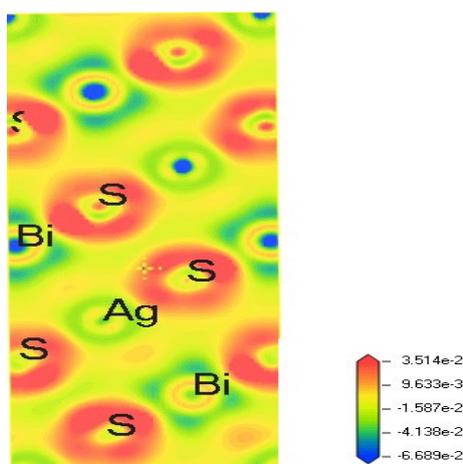


Fig. 4. The calculated electron density difference of β -AgBiS₂ crystal.

Table 2. Mulliken charge (e), bond population (e) and bond lengths of AgBiS₂ (HSE06).

species	s	p	d	Total	Charge(e)
S	1.88	4.69	0	6.57	-0.57
Ag	2.41	6.39	9.96	18.76	0.24
Bi	2.03	2.07	10	14.09	0.91
Bonds	population			Bond length (Å)	
S-Ag	0.38			2.78499	
S-Bi	0.47			2.82514	

3.3. Optical properties

Based on the electronic structure, the optical properties may be obtained from the knowledge of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. In this work, for solar photovoltaic applications, the optical absorption spectrum of β -AgBiS₂ crystal in polycrystalline state is calculated by the PBE and HSE06 methods, respectively. It should be point out that when the PBE method used, we adopted the scissor operator to translate the entire conduction band

upward so that the band gap is consistent with the experimental value of 1.2 eV, which is very close to the band gap of 1.205 eV obtained by the HSE06 methods.

Fig. 5 illustrates the absorption spectrum of β -AgBiS₂ crystal, and it can be seen from the figure that the profiles of the light absorption curves obtained by the two methods are very consistent, as can be seen in Fig. 5a in the energy range of photon energies greater than 1.2 eV up to 4 eV, the light absorption coefficient of the material increases rapidly and the scale of the absorption coefficient reaches 10^5 cm^{-1} , as can be seen in Fig. 5b. in the short wavelength region of visible light, the light absorption coefficient of the material is maintained above 10^5 cm^{-1} . In the long wavelength band of visible light, the light absorption coefficient slowly decreases to a scale of 10^4 cm^{-1} , the same order of magnitude as that of the silicon material [23].

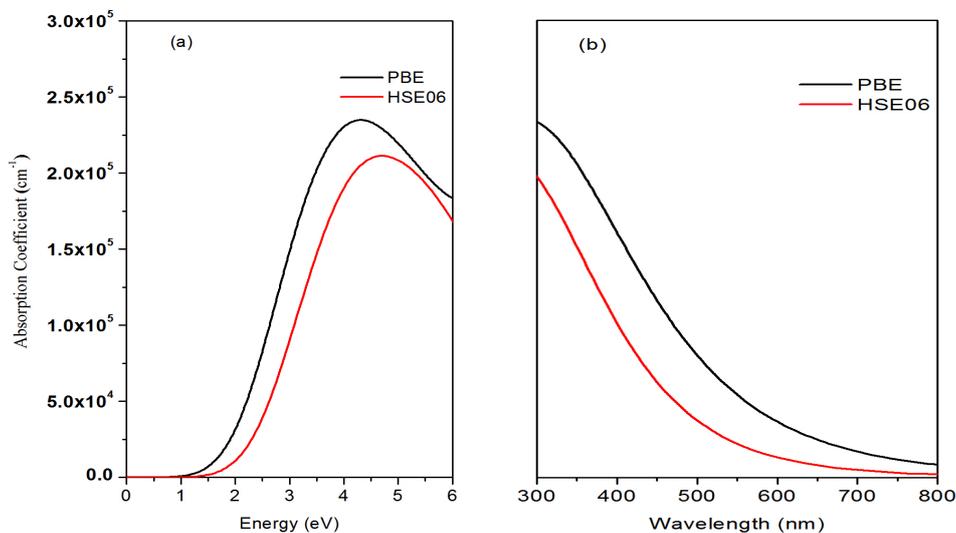


Fig. 5. Absorption spectrum of β -AgBiS₂ crystal.

4. Conclusions

In the current work, we have investigated the electronic band structure, density of states, chemical bonding, and optical absorption properties of β -AgBiS₂ crystal using the first principle calculations, and found that β -AgBiS₂ is an indirect band gap semiconductor, the band gap get by the GGA-PBE method is 0.571 eV, while the band gap obtained with the hybrid functional HSE06 method is 1.205 eV, which is very close to the experimental results.

The material electron difference density map and Mulliken overlap population show that the Ag-S bonds and Bi-S bonds are both ionic bonds. The calculated optical absorption coefficients of β -AgBiS₂ in the range of visible light reached 10^5 cm^{-1} , which prove that β -AgBiS₂ is a promising material for solar photovoltaic conversion.

Acknowledgments

This work was supported by the Foundation of Hunan Double First-rate Discipline Construction Projects of Bioengineering, Huaihua Key Laboratory of Agricultural Ecology Prevention and control, and the Research Learning and Innovative Experimental Program (No. 50) for College Students at Huaihua University.

References

- [1] P. C. Huang, W. C. Yang, M. W. Lee, *The Journal of Physical Chemistry C*, **117** (36), 18308-18314 (2013); <https://doi.org/10.1021/jp4046337>
- [2] M. Bernechea, N. Cates, G. Xercavins, et al., *Nature Photon* **10**, 521–525 (2016); <https://doi.org/10.1038/nphoton.2016.108>
- [3] P. Ganguly, S. Mathew, L. Clarizia, et al., *Applied Catalysis B: Environmental*, **253**, 401-418 (2019); <https://doi.org/10.1016/j.apcatb.2019.04.033>
- [4] Y. Wang, L. Peng, Z. Wang, G. Konstantatos, *Advanced Energy Materials*, **12** (21), 2200700 (2022); <https://doi.org/10.1002/aenm.202200700>
- [5] Y. Guan, Y. Huang, D. Wu, D. Feng, M. He, J. He, *Applied Physics Letters*, **112** (21), 213905 (2018); <https://doi.org/10.1063/1.5034388>
- [6] T. Manimozhi, S. Kavirajan, K. Kamala Bharathi et al., *J Mater Sci: Mater Electron* **33**, 12615–12628, (2022); <https://doi.org/10.1007/s10854-022-08211-y>
- [7] Ajiboye T O, Oyewo O A, Marzouki R, et al., *Ceramics International*, **49** (4), 6149-6163 (2023); <https://doi.org/10.1016/j.ceramint.2022.10.187>
- [8] F. Vines, M. Bernechea, G. Konstantatos, and F. Illas, *Physical Review B*, **94**(23), 235203, (2016); <https://doi.org/10.1103/PhysRevB.94.235203>
- [9] S. Suzuki, M. Tsuyama, *Japanese Journal of Applied Physics*, **59** (4): 041002 (2020).
- [10] A. Tabeti, M. Batouche, K. Bidai, A. Djied, T. Seddik, et al., *Chinese Journal of Physics*, **59**, 578-584 (2019); <https://doi.org/10.1016/j.cjph.2019.04.012>
- [11] M. D. Segall, P. J. D. Lindan, M. J. Probert et al., [*J*]. *Journal of physics: condensed matter*, **14** (11), 2717 (2002).
- [12] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.*, **64** (4), 1046-1077 (1992); <https://doi.org/10.1103/RevModPhys.64.1045>
- [13] J. P. Perdew, K. Burke, M. Ernzerhof, *Physical review letters*, **77**(18), 3865, (1996); <https://doi.org/10.1103/PhysRevLett.77.3865>
- [14] D. Vanderbilt, *Physical review B*, **41**(11), 7892 (1990); <https://doi.org/10.1103/PhysRevB.41.7892>
- [15] J. Heyd, J. E. Peralta, G. E. Scuseria et al., *The Journal of chemical physics*, **123**(17), 174101 (2005); <https://doi.org/10.1063/1.2085170>
- [16] D. R. Hamann, M. Schlüter, C. Chiang, *Physical Review Letters*, **43**(20): 1494, (1979); <https://doi.org/10.1103/PhysRevLett.43.1494>
- [17] S. Geller, J. H. Wernick, *Acta crystallographica*, **12** (1), 46-54 (1959); <https://doi.org/10.1107/S0365110X59000135>

- [18] G. K Balcı, S. Ayhan, International Advanced Researches and Engineering Journal, **2** (1), 1-8 (2018);
- [19] P. Bayliss, American Mineralogist, **76** (1-2), 257-265 (1991).
- [20] I. I. Golovach, V. S. Gerasimenko, V. Y. Slivka et al., Soviet Physics Journal, **19**, 294–298 (1976); <https://doi.org/10.1007/BF00945676>
- [21] B. Pejova, D. Nesheva, Z. Aneva et al., The Journal of Physical Chemistry C, **115**(1) 37-46 (2011); <https://doi.org/10.1021/jp106605t>
- [22] J. P. Perdew, M. Levy, Physical Review Letters, **51** (20), 1884 (1983); <https://doi.org/10.1103/PhysRevLett.51.1884>
- [23] K. Rajkanan, R. Singh, J. Shewchun, Solid State Electronics, **22** (9), 793-795 (1979); [https://doi.org/10.1016/0038-1101\(79\)90128-X](https://doi.org/10.1016/0038-1101(79)90128-X)